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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Polyurethane Dispersions

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Abstract of the disclosure:

Polyurethane dispersions

Polyurethane dispersions prepared by polymerization, initiated by free radicals, of polyurethane macromonomers containing carboxyl, phosphonic acid or sulfonic acid groups, terminal vinyl groups and optionally urethane, thiourethane or urea groups, the terminal vinyl groups not being derived from hydroxyalkyl (meth)acrylates.

These polyurethane dispersions are suitable for the production of coatings on substrates, as adhesives or as binders in printing inks.

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Polyurethane dispersions

Polyurethane dispersions prepared by polymerization, initiated by free radicals, of polyurethane macromonomers containing carboxyl, phosphonic acid or sulfonic acid groups, terminal vinyl groups and optionally urethane, thiourethane or urea groups, the terminal vinyl groups not being derived from hydroxyalkyl (meth)acrylates.

These polyurethane dispersions are suitable for the production of coatings on substrates, as adhesives or as binders in printing inks.

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Polyurethane dispersions

- 5 Aqueous polyurethane dispersions are described in EP
98 752. These polyurethane dispersions are prepared by
first reacting a diol containing ionic groups, a polyol-
polyether or polyol-polyester and an excess of a diiso-
10 cyanate to form a prepolymer. In the second stage, this
prepolymer, which contains free isocyanate groups, is
then reacted with a hydroxy-alkyl (meth)acrylate. This
gives a second prepolymer which contains vinyl groups,
and this prepolymer is then finally polymerized in an
aqueous dispersion using initiators which form free
15 radicals. In the polyurethanes described here, the vinyl
group is achieved exclusively by incorporation of
hydroxy-C₂-C₄-alkyl (meth)acrylates. Incorporation of
other monomers for the formation of vinyl groups is not
mentioned therein.
- 20 The present invention relates to polyurethane dispersions
which are prepared by polymerization, initiated by free
radicals, of polyurethane macromonomers containing
carboxyl, phosphonic acid or sulfonic acid groups, ter-
minal vinyl groups and optionally urethane, thiourethane
25 and/or urea groups, the terminal vinyl groups not being
derived from hydroxy-C₂-C₄-alkyl (meth)acrylates. These
polyurethane macromonomers can be prepared by poly-
addition of polyhydroxy compounds from the group
comprising polyhydroxy-polyethers, polyhydroxy-polyesters
30 and polyhydroxy-polycarbonates, and furthermore
polyhydroxycarboxylic acids, polyhydroxyphosphonic acids
and polyhydroxysulfonic acids, and polyisocyanates.

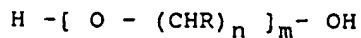
The mixing ratios here are selected so that the
polyisocyanate is in excess, so that the prepolymer

formed contains free isocyanate groups in addition to the carboxyl, phosphonic acid and sulfonic acid groups. In a preferred procedure, it is also possible first to employ the polyisocyanate in a substoichiometric amount, in order
 5 in this way to obtain a prepolymer containing free hydroxyl groups. In an additional step, this prepolymer is then reacted with further polyisocyanate, in order in this way likewise to obtain a prepolymer containing free isocyanate groups.

10 These prepolymers are then further reacted with a monomer containing, in addition to a vinyl group, a group which reacts with isocyanate groups, such as, for example, the hydroxyl, amino or mercapto group. Examples of these are products of the reaction of monoepoxides and α, β -
 15 unsaturated carboxylic acids, such as, for example, products of the reaction of glycidyl versatate and (meth)acrylic acid or 2-ethylhexyl glycidyl ether and (meth)acrylic acid, products of the reaction of α, β -
 20 unsaturated glycidyl esters or ethers with monocarboxylic acids, for example products of the reaction of glycidyl methacrylate and stearic acid or linseed oil fatty acid and furthermore (meth)acrylates containing amino groups, such as, for example, t-butylaminoethyl methacrylate.

These monomers can be used by themselves, but it is also
 25 possible for these monomers to be employed as a mixture with primary or secondary amines, alcohols or thioalcohols. A macromonomer which contains terminal vinyl groups is obtained in this manner. This macromonomer is then polymerized in the last stage via
 30 the vinyl groups using initiators which form free radicals.

Possible polyhydroxy-polyethers are compounds of the formula



in which

- R is hydrogen or a lower alkyl radical, optionally with various substituents,
- n is a number from 2 to 6 and
- 5 m is a number from 10 to 120.

Examples are poly(oxytetramethylene) glycols, poly(oxyethylene) glycols and poly(oxypropylene) glycols.

- 10 The preferred polyhydroxy-polyethers are poly(oxypropylene) glycols having a molecular weight in the range from 400 to 5000.

- 15 The polyhydroxy-polyesters are prepared by esterification of organic polycarboxylic acids or their anhydrides with organic polyols. The polycarboxylic acids and the polyols can be aliphatic or aromatic polycarboxylic acids and polyols.

- 20 The polyols used for the preparation include alkylene glycols, such as ethylene glycol, butylene glycol, hexane-1,6-diol, neopentylglycol and other glycols, such as, for example, dimethylolcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane and trishydroxyalkylalkanes, such as, for example, trimethylolpropane, and tetrakis(hydroxyalkyl)alkanes, such as, for example, pentaerythritol.

- 25 The acid component of the polyester primarily consists of low molecular weight polycarboxylic acids or their anhydrides having 2 to 18 carbon atoms in the molecule.

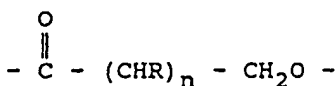
- 30 Suitable acids are, for example, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, hexachloroheptanedicarboxylic acid, alkyl- and alkenylsuccinic acid, for example n-octenylsuccinic acid and n- and iso-dodecenylsuccinic acid, tetrachlorophthalic acid,

trimellitic acid and pyromellitic acid. Instead of these acids, their anhydrides, where these exist, can also be used. Dimeric and trimeric fatty acids can also be employed as the polycarboxylic acids.

- 5 The terms polyhydroxy-polyether and polyhydroxy-polyester are also to be understood as meaning those products of this type which contain monomers having carboxyl, sulfonate or phosphonate groups.

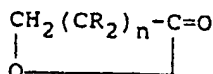
- 10 Polyhydroxy-polyesters which are derived from lactones can furthermore be used in the invention. These products are obtained, for example, by reaction of an ϵ -caprolactone with a polyol. Such products are described in US-PS 3 169 945.

- 15 The polylactone-polyols which are obtained by this reaction are distinguished by the presence of a terminal hydroxyl group and by recurring polyester contents which are derived from the lactone. These recurring molecular contents can correspond to the formula



- 20 in which n is preferably 4 to 6 and the substituent is hydrogen, an alkyl radical, a cycloalkyl radical or an alkoxy radical, no substituent containing more than 12 carbon atoms.

- 25 The lactone used as the starting material can be any desired lactone or any desired combination of lactones, and this lactone should contain at least 6 carbon atoms in the ring, for example 6 to 8 carbon atoms, and 2 hydrogen substituents should be present on the carbon atom bonded to the oxygen group of the ring. The lactone
30 used as the starting material can be represented by the following general formula:

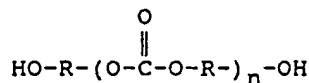


in which n and R have the meaning already given.

The lactones preferred in the invention are the ϵ -caprolactones, in which n has the value 4. The most preferred lactone is unsubstituted ϵ -caprolactone, in which n has the value 4 and all the R substituents are hydrogen. This lactone is particularly preferred, since it is available in large amounts and produces coatings which have excellent properties. Various other lactones can furthermore be used individually or in combination.

Examples of aliphatic polyols which are suitable for the reaction with the lactone are ethylene glycol, 1,3-propanediol, 1,4-butanediol, hexane-1,6-diol, dimethylolcyclohexane, trimethylolpropane and pentaerythritol.

Possible starting compounds are furthermore polycarbonate-polyols and polycarbonate-diols which correspond to the general formula



where R is an alkylene radical. These OH-functional polycarbonates can be prepared by reaction of polyols, such as propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, diethylene glycol, triethylene glycol, 1,4-bis-hydroxymethylcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, neopentylglycol, trimethylolpropane or pentaerythritol, with di-carbonates, such as dimethyl, diethyl or diphenyl carbonate, or phosgene. Mixtures of such polyols can likewise be employed.

- The polyhydroxy-polyethers, polyhydroxy-polyesters and polyhydroxy-polycarbonates described above can be employed together. These polyhydroxy compounds can moreover also be employed together with various amounts
- 5 of low molecular weight isocyanate-reactive polyols, polyamines or polymercaptans. Possible compounds of this type are, for example, ethylene glycol, butanediol, pentaerythritol, trimethylolpropane, ethylenediamine, propylenediamine and hexamethylenediamine.
- 10 Low molecular weight polyols, preferably diols, which moreover also contain an ionic group in the form of the carboxylic acid, phosphonic acid or sulfonic acid group are employed as a further unit for the preparation of the polyurethane dispersions according to the invention.
- 15 Examples of this group of monomers are α -C₂-C₁₀-bis-hydroxycarboxylic acids, such as, for example, dihydroxypropionic acid, dimethylolpropionic acid, dihydroxyethylpropionic acid, dimethylolbutyric acid, dihydroxysuccinic acid and dihydroxybenzoic acid, or 3-hydroxy-2-hydroxy-
- 20 methylpropanesulfonic acid and 1,4-dihydroxybutanesulfonic acid.

These monomers can be neutralized before the reaction with a tertiary amine, such as, for example, trimethylamine, triethylamine, dimethylaniline, diethyl-

25 aniline or triphenylamine, in order to avoid reaction of the acid group with the isocyanate. If the probability of such a reaction is only slight, the acid groups can also be neutralized only after their incorporation into the polyurethane microgel. The neutralization is then carried

30 out with aqueous solutions of alkali metal hydroxides or with amines, for example with trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, aminomethylpropanol, dimethylaminomethylpropanol and

35 dimethylisopropanolamine, or with ammonia. In addition, the neutralization can also be carried out with mixtures

of amines and ammonia.

Examples of suitable polyisocyanates are trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylethylene diisocyanate, 2,3-dimethylethylenediisocyanate, 1-methyltrimethylene diisocyanate, cyclopentylene 1,3-diisocyanate, cyclohexylene 1,4-diisocyanate, cyclohexylene 1,2-diisocyanate, phenylene 1,3-diisocyanate, phenylene 1,4-diisocyanate, toluylene 2,4-diisocyanate, toluylene 2,6-diisocyanate, biphenylene 4,4'-diisocyanate, naphthylene 1,5-diisocyanate, naphthylene 1,4-diisocyanate, 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, bis-(4-isocyanatocyclohexyl)-methane, bis-(4-isocyanatocyclophenyl)methane, 4,4'-diisocyanatodiphenyl ether, 2,3-bis-(8-isocyanatooctyl)-4-octyl-5-hexylcyclohexene, tetramethylxylylene diisocyanates, trimethylhexamethylene diisocyanates, isocyanurates of the above diisocyanates or allophanates of the above diisocyanates. Mixtures of such di- or polyisocyanates can likewise be employed.

It is of particular importance for the polyurethane dispersions according to the invention that the macromonomers which lead to these dispersions contain terminal vinyl groups. The term terminal vinyl groups is intended to mean those vinyl groups which hang on the start or end of the polymer chain. Terminal vinyl groups are incorporated by reacting a prepolymer obtained by reaction of the polyols and the polyhydroxycarboxylic, polyhydroxyphosphonic or polyhydroxysulfonic acids and containing free isocyanate groups with a vinyl monomer of the abovementioned type which contains a group which is reactive toward isocyanate groups.

The macromonomers built up from these monomers can additionally also be modified by incorporating amines, alcohols and/or thioalcohols. For this modification, the

- intermediate product produced in the first stage, which contains terminal isocyanate radicals, is reacted not by itself with the vinyl monomer which contains an isocyanate-reactive group, but this monomer is reacted
- 5 together with amines, alcohols and/or thioalcohols. Possible reactants here are, for example, primary amines, such as propylamine, butylamine, pentylamine, 2-amino-2-methylpropanol, ethanolamine and propanolamine; secondary
- 10 amines, such as diethanolamine, dibutylamine and diisopropanolamine; primary alcohols, such as methanol, ethanol, propanol, butanol, hexanol, dodecanol and stearyl alcohol; and secondary alcohols, such as isopropanol and isobutanol, and the corresponding thioalcohols.
- 15 The preparation of the intermediate products in the first stages is carried out by the customary methods which are known in urethane chemistry. Tertiary amines, such as, for example, triethylamine, dimethylbenzylamine and diazabicyclooctane, and dialkyltin(IV) compounds, such
- 20 as, for example, dibutyltin dilaurate, dibutyltin dichloride and dimethyltin dilaurate, can be employed as catalysts here. The reaction takes place in the melt without a solvent, in the presence of a solvent or in the presence of a so-called reactive diluent. Possible
- 25 solvents are those which can be removed later by distillation, for example dioxane, methyl ethyl ketone, methyl isobutyl ketone, acetone, tetrahydrofuran, toluene and xylene. These solvents can be completely or partly distilled off after the preparation of the polyurethane
- 30 macromonomers or after the free radical polymerization. In addition, the reaction can also be carried out in a high-boiling water-dilutable solvent, for example in N-methylpyrrolidone, this then remaining in the dispersion. Further solvents, such as, for example,
- 35 glycol ethers and esters thereof, can also be added before the dispersing process. Suitable glycol ethers are, for example, butylglycol, butyldiglycol,

methoxypropanol, dipropylene glycol monomethyl ether or diglycol dimethyl ether. The reactive diluents are α, β -unsaturated monomers, which are copolymerized with the macromonomers containing vinyl groups in the final stage.

- 5 Examples of such reactive diluents are α, β -unsaturated vinyl monomers, such as alkyl acrylates, methacrylates and crotonates having 1 to 20 carbon atoms in the alkyl radical, di-, tri- and tetraacrylates, -methacrylates and -crotonates of glycols, tri- and tetrafunctional
- 10 alcohols, substituted and unsubstituted acryl- and methacrylamides, vinyl ethers, α, β -unsaturated aldehydes and ketones, vinyl alkyl ketones having 1 to 20 carbon atoms in the alkyl radical, vinyl ethers, vinyl esters, diesters of α, β -unsaturated dicarboxylic acids, styrene
- 15 and styrene derivatives, such as, for example, α -methylstyrene.

- The intermediates obtained in this way from the first step are then reacted, without intermediate isolation, under the same conditions with the isocyanate-reactive
- 20 vinyl monomers, where amines, alcohols or thioalcohols are also suitable, as mentioned above, in addition to the isocyanate-reactive vinyl monomers. The mixing ratios are selected in each case so that all the isocyanate groups are converted into urethane, thiourethane or urea groups.

- 25 The macromonomers thus obtained are then neutralized, if the acid groups in the monomers which carry such groups have not already been employed in the neutralized form from the beginning. The neutralization is then carried out with aqueous solutions of alkali metal hydroxides or
- 30 with amines, for example with trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, aminomethylpropanol, dimethylaminomethylpropanol or dimethylisopropanolamine, or with ammonia. In addition,
- 35 the neutralization can also be carried out with mixtures of amines and ammonia.

To prepare the polyurethane dispersions according to the invention, macromonomers which contain vinyl groups are converted into an aqueous dispersion by addition of water and polymerized by methods which are known per se using
5 initiators which form free radicals. If so-called reactive diluents are not present from the beginning, monomers of this type, as described above, can be incorporated into the polyurethane as copolymerized units during this polymerization. Carboxyl-, hydroxyl-, amino-,
10 ether- and mercapto-functional α,β -unsaturated vinyl monomers can also furthermore additionally be added immediately before or during the free radical polymerization. Examples of these are hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate,
15 meth(acrylic) acid, crotonic acid, glycidyl (meth)acrylate, t-butylaminoethyl methacrylate and dimethylaminoethyl methacrylate. The content of copolymerized vinyl monomers is 0 to 95% by weight, preferably 5 to 70% by weight, based on the solid of the
20 polyurethane dispersion. The ratio of flexible and rigid segments in the polyurethane macromonomers is 0.30 to 6, particularly preferably 0.8 to 3. Possible initiators for the polymerization are the known initiators which form free radicals, such as ammonium peroxydisulfate,
25 potassium peroxide-sulfate, sodium peroxide-sulfate, hydrogen peroxide, organic peroxides, such as, for example, cumene hydroperoxide, t-butyl hydroperoxide, di-tert-butyl peroxide and dioctyl peroxide, tert-butyl perpivalate, tert-butyl perisononanoate, tert-butyl
30 perethylhexanoate, tert-butyl perneodecanoate, di-2-ethylhexyl peroxydicarbonate, diisotridecyl peroxydicarbonate and azo compounds, such as, for example, azo-bis(isobutyronitrile) and azo-bis(4-cyanovaleric acid), or the customary redox systems, for
35 example sodium sulfite, sodium dithionite and ascorbic acid and organic peroxides or hydrogen peroxide. Regulators (mercaptans), emulsifiers, protective colloids and other customary auxiliaries can moreover also be

added.

5 If the preparation of the macromonomer has been carried out in a solvent which can be removed by distillation and either forms an azeotrope with water or can be fractionated out of the aqueous phase, for example in acetone, dioxane, methyl ethyl ketone, methyl isobutyl ketone, tetrahydrofuran, toluene or xylene, this solvent is removed from the dispersion by distillation. Aqueous polyurethane dispersions are obtained in all cases.

10 The acid numbers of these polyurethanes are in the range from 5 to 80, particularly preferably in the range from 10 to 40 units.

15 Further details on the preparation of the macromonomers and polymerization thereof to give the polyurethane dispersions according to the invention can be seen from the following general process descriptions. These process conditions are preferred embodiments.

1. Solvent-free

a. without an auxiliary solvent

20 At temperatures of 100 to 150°C, particularly preferably 120 to 135°C, the polyhydroxy acid and if appropriate low molecular weight polyols are dissolved in a polyol having an average molecular weight of 400 to 5000 and reacted with a polyisocyanate or polyisocyanate mixtures to give
25 a product which has OH end groups and has an average molecular weight (Mn) of 500 to 12,000, particularly preferably 600 to 8000. After the product has been cooled to a temperature of 30 to 100°C, particularly preferably 50 to 80°C, a comonomer which is not isocyanate-reactive
30 is added. A resin containing terminal NCO groups is built up at this temperature by further addition of polyisocyanate, and the product is then reacted with a monofunctional, NCO-reactive vinyl compound to give a polyurethane macromonomer having an average molecular

weight of 700 to 24,000, particularly preferably 800 to 16,000. This resulting resin solution is neutralized with amines or other bases and dispersed in water. Other vinyl comonomers can also be added to the resulting dispersion before or during the free radical polymerization which is still to be carried out. The free vinyl compounds are then polymerized in the aqueous dispersion using initiators which form free radicals, at a temperature of 0 to 95°C, particularly preferably 40 to 95°C, and at a temperature of 30 to 70°C if redox systems are used. A solvent-free polyurethane dispersion is formed here.

b. with an auxiliary solvent

In contrast to process 1.a., in this case all the polyol components are dissolved in a solvent which can be fractionated out of the aqueous phase or forms an azeotrope with water and are reacted directly with polyisocyanate or polyisocyanate mixtures to give the product which contains terminal NCO groups. The solvent content is 1 to 80% by weight, particularly preferably between 10 and 50% by weight, based on the solid of the polyurethane macromonomer. The temperature for this step is between 30 and 100°C, particularly preferably between 50 and 80°C. After the reaction with a monofunctional, isocyanate-reactive vinyl compound to give a polyurethane macromonomer having a molecular weight of 500 to 30000, particularly preferably 700 to 20000, the product is neutralized with amines or other bases and dispersed in water. The auxiliary solvent is then distilled off from the aqueous phase, if necessary under a slight vacuum. Vinyl comonomers can also be added to this solvent-free dispersion before or during the free radical polymerization which is still to be carried out. Polymerization is then carried out with initiators which form free radicals, at a temperature of between 0 and 95°C, particularly preferably between 40 and 95°C, and at a temperature of 30 to 70°C if redox systems are used, to give a solvent-free polyurethane dispersion.

2. Containing solvent

If a non-distillable auxiliary solvent, such as, for example, N-methylpyrrolidone, is used, the procedure is exactly as in process 1.b., but the distillation after the dispersing operation is omitted. If appropriate vinyl monomers can here be added before or during the polymerization. The polymerization is carried out as in process 1.b. The solvent content is in the range from 0.1 to 30% by weight, particularly preferably 1 to 15% by weight, based on the total binder dispersion.

Because of their chemical build-up, the polyurethane dispersions according to the invention are suitable for diverse uses, for example for the preparation of coating systems, inter alia for coating wood, as binders for water-dilutable adhesives or as resins for printing inks.

They can be combined with and are in general compatible with other aqueous dispersions and solutions of plastics, for example acrylic and/or methacrylic polymers, polyurethane, polyurea resins, polyester resins and epoxy resins, thermoplastics based on polyvinyl acetate, -vinyl chloride, -vinyl ether, -chloroprene and -acrylonitrile and ethylene/butadiene/styrene copolymers. They can also be combined with substances which have a thickening action and are based on polyacrylates or polyurethanes containing carboxyl groups, hydroxyethylcellulose, polyvinyl alcohols and inorganic thixotropic agents, such as bentonite, sodium/magnesium silicates and sodium/magnesium/fluorine/lithium silicates.

The polyurethane dispersions according to the invention can be applied to the most diverse substrates, for example ceramic, wood, glass, concrete and preferably plastics, such as polycarbonate, polystyrene, polyvinyl chloride, polyester, poly(meth)acrylates, acrylonitrile/butadiene/styrene polymers and the like, and preferably to metal, such as iron, copper, aluminum, steel, brass,

bronze, tin, zinc, titanium, magnesium and the like. They adhere to the various substrates without adhesion-promoting primers or intermediate layers.

5 The polyurethane dispersions according to the invention are suitable, for example, for the production of corrosion-preventing coatings and/or intermediate coatings for the most diverse fields of use, in particular for the production of metallic and solid base paints in multi-coat build-ups of paint for the fields of painting of automobiles and plastics, and for producing primer paints for the field of painting of plastics.

10 Because of the short flush-off times of the base paints based on the polyurethane dispersions according to the invention, the pigmented coat of base paint can be over-
15 varnished with a clear varnish without a stoving step (wet-in-wet process) and the coatings can then be stoved together or subjected to forced drying. Base paints prepared with the polyurethane dispersions according to the invention give paint films of the same quality
20 largely independently of the stoving or drying temperature, so that they can be employed both as a repair paint for motor vehicles and as a stoving paint for series painting of motor vehicles. In both cases, paint films having a good adhesion to the original coating and a good
25 resistance to condensation water result. The brilliance of the paint coating after a condensation water test is furthermore not noticeably impaired.

The crosslinking agents customary in the paint industry, such as, for example, water-soluble or -emulsifiable
30 melamine or benzoguanamine resins, polyisocyanates or prepolymers having terminal isocyanate groups, water-soluble or -dispersible polyaziridines and blocked polyisocyanates, can be added during formulation of water-dilutable paints using the polyurethane dispersions
35 according to the invention. The aqueous coating systems

can contain all the pigments and dyestuffs, which can be of an inorganic or organic nature, which are known and are customary in paint technology, as well as wetting agents, foam suppressants, flow control agents, stabilizers, catalysts, fillers, plasticizers and solvents.

The polyurethane dispersions according to the invention can also be used directly for gluing any desired substrates. To achieve specific adhesive properties, the polyurethane dispersions according to the invention can be mixed with other dispersions or solutions of plastics (see above). Crosslinking agents, such as, for example, polyisocyanates or prepolymers having terminal isocyanate groups or water-soluble or -emulsifiable melamine or benzoguanamine resins, can furthermore be added to improve the resistance to heat and peeling.

The adhesives based on the polyurethane dispersions according to the invention can contain the additives customary in adhesives technology, such as plasticizers, solvents, film-binding auxiliaries, fillers and synthetic and naturally occurring resins. They are specifically suitable for the production of gluings of substrates in the motor vehicle industry, for example gluing of interior finishings, and in the shoe industry, for example for gluing the shoe sole and shoe shaft. The adhesives based on the polyurethane dispersions according to the invention are prepared and processed by the customary methods of adhesives technology used for aqueous dispersion and solution adhesives.

Example 1:

258.4 g of a polyester prepared from hexane-1,6-diol and isophthalic and adipic acid and having a hydroxyl number of 84 and an acid number of less than 4 are heated to 130°C together with 23.3 g of dimethylolpropionic acid and 0.4 g of hexane-1,6-diol and the mixture is kept at

this temperature until a homogeneous solution exists. 57.3 g of tetramethylxylylene diisocyanate are then metered in over a period of 15 to 20 minutes, while stirring, and stirring is continued at 130°C until free isocyanate groups are no longer present.

After cooling to 70°C, a solution consisting of 80.0 g of methyl methacrylate and 0.1 g of 2,6-di-tert-butyl-4-methylphenol is added rapidly and the mixture is homogenized. 62.9 g of tetramethylxylylene diisocyanate are then added over a period of 15 minutes and the components are reacted at 70°C until the content of free isocyanate groups is 2.12% by weight, based on the total weight. 93.7 g of a reaction product of glycidyl versatate with methacrylic acid are then metered in rapidly over a period of 15 minutes. The reaction is continued at a temperature of 70°C until free isocyanate groups are no longer present. After addition of 12.4 g of triethylamine, the mixture is homogenized for 5 minutes. 1135 g of water having a temperature of 95°C are then added to the prepolymer solution, while stirring intensively. After cooling to 80°C, the mixture is stirred for a further hour. 10% by volume of an ammonium peroxodisulfate solution consisting of 0.8 g of ammonium peroxodisulfate and 50 g of water are added at 80°C to the dispersion thus prepared. The remaining amount of the ammonium peroxodisulfate solution is metered in over a period of 30 minutes.

The temperature is then kept at 78 to 80°C for a further 2 hours.

After cooling to room temperature, the dispersion is filtered through a 5 μ m filter. The resulting dispersion has a solids content of 32.3% and a pH of 7.50.

Example 2:

282.8 g of a polyester prepared from neopentylglycol, hexane-1,6-diol and isophthalic and adipic acid and having a hydroxyl number of 37 and an acid number of less than 3 are dissolved under reflux in 150 g of acetone together with 28.0 g of dimethylolpropionic acid and 3.3 g of butane-1,4-diol. 112.0 g of 4,4-dicyclohexylmethane diisocyanate are then metered in over a period of 45-60 minutes and the mixture is stirred at the reflux temperature until the content of free isocyanate groups is 1.29% by weight, based on the total weight.

0.1 g of 2,6-di-tert-butyl-4-methylphenol and 67.8 g of a reaction product of glycidyl versatate with methacrylic acid are then added to the prepolymer solution thus obtained. The reaction is continued at the reflux temperature until free isocyanate groups are no longer present. After addition of 18.0 g of triethylamine, 1108 g of water having a temperature of 80°C are added to the polymer solution, while stirring intensively. The acetone solvent is then separated off from the resulting dispersion by vacuum distillation. After addition of 80.0 g of methyl methacrylate, the temperature is increased to 80°C and the mixture is stirred for a further 30 minutes. 10% by volume of an ammonium peroxodisulfate solution consisting of 1.0 g of ammonium peroxodisulfate and 50 g of water is then added at 80°C. The remaining amount of the ammonium peroxodisulfate solution is metered in over a period of 30 minutes. The temperature is kept at 78, to 80°C for a further 2 hours.

After cooling to room temperature, the dispersion is brought to a solids content of 30% and filtered through a 5 μ m filter. The resulting dispersion has a pH of 7.25.

Example 3:

282.8 g of a polyester prepared from 1,6-hexanediol, isophthalic acid and adipic acid, having a hydroxyl number of 84 and an acid number of 4, are dissolved, together with 28.0 g of dimethylolpropionic acid and 0.7 g of 1,4-butanediol, in 105.0 g of N-methylpyrrolidone at 70°C. 114.5 g of isophorone diisocyanate are then metered in with stirring over a period of from 25 to 30 minutes, and stirring is continued at 70°C until the isocyanate content is 1.40% by weight, based on the total weight of the starting materials.

67.8 g of a reaction product of glycidyl versatate and methacrylic acid, and 0.1 g of 2,6-di-tert.-butyl-4-methylphenol are added rapidly to the prepolymer solution thus obtained, and the mixture is homogenized. The reaction is continued at 70°C until free isocyanate groups are no longer present. After addition of 17.0 g of triethylamine, the mixture is homogenized for 5 minutes. 1022 g of water having a temperature of 95°C are then added to the prepolymer solution while stirring intensively. After cooling to 80°C, 80.0 g of methyl methacrylate are added, and the mixture is stirred for a further 60 minutes. 10% by volume of an ammonium peroxodisulfate solution, comprising 1.0 g of ammonium peroxodisulfate and 50 g of water, are added at 80°C to the dispersion thus obtained. The remaining amount of the ammonium peroxodisulfate solution is metered in over a period of 30 minutes.

The temperature is subsequently kept at 78 to 80°C for a further 2 hours. After cooling to room temperature, the dispersion is filtered through a 5 μ m filter. The resulting dispersion has a solids content of 33.3% and a pH of 7.35.

The reaction product of glycidyl versatate with methacrylic acid used in Examples 1 to 3 was prepared as

follows:

784.5 g of glycidyl versatate are homogenized with 258.3 g of methacrylic acid, 0.2 g of 2,6-di-tert.-butyl-4-methylphenol and 1.04 g of AMC-2 (chromium octanoate) at RT. The reactants are then reacted at a temperature of 90°C until the acid number is less than 1 and the epoxide equivalent weight is greater than 10000, based on the total weight of starting materials.

Example 4:

286 g of a poly(butanediol adipate) (OH number: 45) is heated to 130°C together with 23.1 g of dimethylol-propionic acid, and the components are reacted with 30 g of toluylene diisocyanate at this temperature. After cooling to 65-70°C, the mixture is dissolved in 50 g of stabilized methyl methacrylate, together with 4.7 g of hexane-1,6-diol, and reacted with 40.6 g of toluylene diisocyanate at 65-70°C. The product is reacted with the molar amount of the addition product of glycidyl versatate and methacrylic acid which corresponds to the free NCO content. The mixture is then neutralized with 12.7 g of triethylamine and dispersed with 683 g of deionized water. 50 g of a 2% strength by weight aqueous solution of ammonium peroxodisulfate are metered into this dispersion at 80°C and the mixture is subsequently stirred. The resulting dispersion has a solids content of 40% by weight, a pH of 7.2 and a dynamic viscosity of 9 mPas.

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Patent Claims:

1. A polyurethane dispersion prepared by polymerization, initiated by free radicals, of polyurethane macromonomers containing carboxyl, phosphonic acid or sulfonic acid groups, terminal vinyl groups and optionally urethane, thiourethane or urea groups, the terminal vinyl groups not being derived from hydroxy-C₂-C₄-alkyl (meth)acrylates.
2. A polyurethane dispersion as claimed in claim 1, prepared by polymerization of polyurethane macromonomers which contain carboxyl, phosphonic acid or sulfonic acid groups as well as terminal vinyl groups and optionally urethane, thiourethane or urea groups and are obtained by polyaddition of polyhydroxy-polyethers, polyhydroxy-polyesters or polyhydroxy-polycarbonates, polyhydroxycarboxylic acids, polyhydroxyphosphonic acids or polyhydroxysulfonic acids, and polyisocyanates, and subsequent reaction with a monomer which, in addition to at least one vinyl group, also contains a group which reacts with isocyanate groups, with the exception of hydroxy-C₂-C₄-alkyl (meth)acrylates, optionally together with primary or secondary amines, alcohols or thioalcohols.
3. A polyurethane dispersion as claimed in claim 1, prepared by polymerization, initiated by free radicals, in a mixture of water and an organic solvent which is inert toward isocyanate groups, if appropriate in the presence of unsaturated monomers which can be copolymerized with the polyurethane macromonomers, and if appropriate removal of the organic solvent by distillation before or after the free radical polymerization.
4. A polyurethane dispersion as claimed in claim 1, wherein the polyhydroxy-polyethers, polyhydroxy-poly-

esters or polyhydroxy-polycarbonates can contain carboxyl, phosphonic acid or sulfonic acid groups.

5. A polyurethane dispersion as claimed in claim 1, prepared by polymerization, initiated by free radicals, in an unsaturated monomer which serves as the solvent and is copolymerizable with the polyurethane macromonomers, if appropriate in the presence of further copolymerizable unsaturated monomers.
6. The use of a polyurethane dispersion as claimed in claim 1 for the production of coatings on substrates, as an adhesive or as a binder in printing inks.
7. The use of a polyurethane dispersion as claimed in claim 1 for the preparation of metallic and solid base paints in multi-coat build-ups of paint.

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